

# PATENT ABSTRACTS OF JAPAN

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(22)Date of filing : 11.08.2000

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## (54) MANUFACTURING METHOD OF SILICON WAFER

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide the manufacturing method of a silicon wafer which is favorable for forming an annealing wafer uniformly having full zero defects layers and the BMDs density within the surface of the annealing wafer suppressing an irregularity (that is, an irregularity in defect sizes within the surface of the annealing wafer in growing condition) in the zero defects layers, which are seen in the annealing wafer subsequent to a heat treatment within the surface of the annealing wafer and an irregularity in the BMDs density subsequent to a heat treatment, such as a precipitation heat treatment or a device heat treatment, within the surface of the annealing wafer, and to provide such the silicon wafer.

**SOLUTION:** In the manufacturing method of a silicon wafer which forms the silicon wafer from a silicon single crystal pulled up after nitrogen is doped to the silicon single crystal by a CZ method and heat-treats the wafer, the wafer is grown on the condition that the ratio  $V/G$  of the pulling-up speed  $V$  (mm/min) at the time when the silicon single crystal is pulled up to a temperature gradient  $G$  (K/mm) in a solid-liquid interface is set in the ratio of 1 to 0.175 to 0.225 mm<sup>2</sup>/K.min in the extent wider than 90% in the radial direction of the pulled-up crystal and the wafer is formed by the manufacturing method.

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CLAIMS

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[Claim(s)]

[Claim 1] In the manufacture approach of the silicon wafer which produces a silicon wafer from the silicon single crystal which doped nitrogen with the Czochralski method and was able to be pulled up, and heat-treats to this silicon wafer the ratio of the raising rate  $V$  at the time of pulling up said silicon single crystal (mm/min), and the temperature gradient  $G$  of a solid-liquid interface (K/mm) --  $V/G$  The manufacture approach of the silicon wafer characterized by raising on the conditions which serve as  $0.175-0.225\text{mm}^2 / \text{K-min}$  in 90% or more of range of the direction of the diameter of a pull-up crystal.

[Claim 2] the nitrogen concentration in said silicon wafer --  $1 \times 10^{13}-5 \times 10^{15}$  piece/cm<sup>3</sup> it is -- the manufacture approach of a silicon wafer of having indicated things to claim 1 by which it is characterized.

[Claim 3] The silicon wafer characterized by being manufactured by the manufacture approach indicated to said claim 1 or claim 2.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] By heat-treating to the silicon wafer produced from the Czochralski method (CZ process) silicon single crystal which doped and pulled up nitrogen (annealing), this invention has a defect-free layer in the wafer surface section, and relates to the manufacture approach of a suitable silicon wafer to manufacture the silicon wafer (annealing wafer) with which an intrinsic gettering (IG, Intrinsic Gettering) layer is formed in the bulk section.

[0002]

[Description of the Prior Art] The consolidation of much more integrity of a wafer surface and the gettering capacity in bulk is strongly demanded with high integration and detailed-izing of a semiconductor device. The wafer which filled two above-mentioned demands simultaneously was developed by heat-treating to it recently to the CZ process silicon wafer which doped nitrogen.

[0003] Namely, since the size of the grown-in (grown-in) defect under as-grown crystal (void defect mainly formed with the aggregate of an atomic hole) becomes small by doping nitrogen to a CZ process silicon single crystal, According to the precipitation-of-oxygen facilitatory effect which nitrogen moreover has in the bulk section by defect-free-ization of the wafer surface section becoming easy by elevated-temperature annealing of an after process By passing through precipitation heat treatment or a device heat treatment process, IG layer which has the defect (hereafter referred to as BMD (Bulk Micro Defects)) of the oxygen sludge contributed to gettering in high density is formed.

[0004]

[Problem(s) to be Solved by the Invention] By the way, it is formed in the bulk section of a CZ process silicon wafer, and having field interior division cloth is usually known, especially, a BMD consistency and the grown-in defect size of the consistency of BMD which contributes to gettering, and the size of the grown-in defect which influences formation of the defect-free layer of the surface section are large near the core of a wafer, and they have the inclination for both to fall gradually around a wafer.

[0005] This inclination is the same also in a nitrogen dope crystal, and although the absolute value of a BMD consistency or grown-in defect size changes, there is no change in having field interior division cloth. Therefore, especially after giving elevated-temperature annealing for forming a defect-free layer in the surface section, a grown-in defect will tend to remain in a part for the core of an annealing wafer.

[0006] Moreover, it became clear by examination of this invention person that the inclination for a BMD consistency to fall by the wafer periphery is remarkable about especially a nitrogen dope wafer about the BMD consistency after the precipitation heat treatment which determines the gettering capacity of bulk.

[0007] Thus, it has the problem that any property of the BMD consistency after the defect-free layer formed in the wafer surface section for which an annealing wafer is asked, precipitation heat treatment, or device heat treatment is uneven in a field at present.

[0008] Then, it is what was made in order that this invention might solve such a trouble. The variation within a field of the defect-free layer looked at by the annealing wafer after heat treatment (namely, variation within a field of grown-in defect size), The variation within a field of the BMD consistency after heat treatment of precipitation heat treatment or device heat treatment is suppressed. In order to produce the annealing wafer which has sufficient defect-free layer and a BMD consistency in the homogeneity within a field, it sets it as the main object to offer the approach and such a silicon wafer which manufacture a suitable silicon wafer.

[0009]

[Means for Solving the Problem] Invention concerning the manufacture approach of the silicon wafer of this

invention of attaining the above-mentioned object In the manufacture approach of the silicon wafer which produces a silicon wafer from the silicon single crystal which doped nitrogen with the Czochralski method and was able to be pulled up, and heat-treats to this silicon wafer the ratio of the raising rate  $V$  at the time of pulling up said silicon single crystal (mm/min), and the temperature gradient  $G$  of a solid-liquid interface (K/mm) --  $V/G$  It is characterized by raising on the conditions which serve as  $0.175\text{--}0.225\text{mm}^2 / \text{K}\cdot\text{min}$  in 90% or more of range of the direction of the diameter of a pull-up crystal (claim 1).

[0010] The silicon wafer cut down from the silicon single crystal which doped the nitrogen raised under such conditions can also make the field interior division cloth of grown-in defect size what also has the uniform field interior division cloth of a BMD consistency. Therefore, if elevated-temperature heat treatment is performed to this, there is no variation within a field of the defect-free layer of the wafer surface section, and the BMD consistency of the bulk section can obtain the high annealing wafer of uniform and high-density IG capacity in a field.

[0011] in this case, the nitrogen concentration in said silicon wafer --  $1 \times 10^{13}\text{--}5 \times 10^{15}$  piece/cm<sup>3</sup> it is -- things are desirable (claim 2). Since it does not have an adverse effect on training of a single crystal, either, while the effectiveness which makes size of a grown-in defect small is enough, if nitrogen concentration is dedicated within such limits, while defect-free-ization of the wafer surface section becomes easy by elevated-temperature annealing of an after process, IG layer which has BMD which contributes to gettering in high density can be formed by passing through precipitation heat treatment or device heat treatment according to the precipitation-of-oxygen facilitatory effect which nitrogen has in the bulk section.

[0012] And according to this invention, the variation within a field of the defect-free layer looked at by the annealing wafer after heat treatment and the variation within a field of the BMD consistency after heat treatment of precipitation heat treatment or device heat treatment are suppressed, and the silicon wafer which can obtain the annealing wafer which has sufficient defect-free layer and a BMD consistency in the homogeneity within a field is offered (claim 3).

[0013] Hereafter, this invention is further explained to a detail. this invention person did the knowledge of preparing that in which neither the consistency of BMD which contributes to the gettering formed in the bulk section as a silicon wafer, nor the size of the grown-in defect which influences formation of the defect-free layer of the surface section has field interior division cloth, in order to produce the annealing wafer which has sufficient defect-free layer and a BMD consistency in the homogeneity within a field.

[0014] That is, this invention person investigated wholeheartedly about the grown-in defect consistency of the wafer surface section after giving elevated-temperature annealing to the CZ process silicon wafer which is carrying out actual condition manufacture as an object for annealing wafers and by which the nitrogen dope was carried out, and the BMD consistency after additional \*\*\*\*. Consequently, although there were many residual defects and its BMD consistency was also high in the wafer core, in the wafer periphery, the number of residual defects was understood that it is few and there are also few BMD consistencies.

Moreover, the middle location (henceforth  $R/2$  location)  $R$  also had few residual defects moderately in the wafer radius, and the BMD consistency was also high moderately.

[0015] In these three places, the integrity of the surface section and the balance of the gettering capacity in bulk will have  $R/2$  best location. That is, if the condition of this  $R/2$  location is expandable in a wafer side, a uniform and quality wafer will be obtained in a field. Then, in order to expand the condition of this  $R/2$  location, the correlation with an approach to pull up distribution of BMD or a grown-in defect and a CZ process silicon single crystal was investigated.

[0016] Consequently, as for the cause by which the field interior division cloth of grown-in defect size or a BMD consistency becomes an ununiformity in this way,  $V/G$  which is the ratio of the temperature gradient  $G$  (K/mm) of the solid-liquid interface of the raising shaft orientations in the range from the pull-up rate  $V$  at the time of crystal training (mm/min) and the melting point of silicon to 1400 degrees C at least had distribution in the field, namely, it has turned out that it is to change  $V/G$  in a field. Then, it decided to calculate concrete  $V/G$  value required in order not to be concerned with the location within a wafer side but to make grown-in defect size and a BMD consistency into a desired thing. Hereafter, this is explained.

[0017] Since it is already known well that a grown-in defect will be influenced of  $V/G$  the specific hot zone (it Zone(s) and HZ(s) Hot [ ] --) of crystal pulling equipment It is the nitrogen concentration incorporated during a pull-up crystal using the structure in a furnace  $1 \times 10^{13}$  pieces/cm<sup>3</sup> It carries out. The crystal of two or more was raised at the pull-up rate chosen from the range of 1.0 - 1.4 mm/min, and the relation between the relation between the field interior division cloth of each  $V/G$  and the size of a grown-in defect and the BMD consistency after heat treatment of 800 degree-Cx4-hour +1000-degree-Cx 16 hours was investigated. The result is shown in drawing 1 and drawing 2.

[0018] It means that drawing 1 shows the relation of all the data of a BMD consistency and V/G which were measured about a center section, the R/2 section within the field of a wafer, and a periphery (it is the location of 10mm from a wafer periphery), and the BMD consistency correlates it V/G and directly.  $1 \times 10^9$  which will become inadequate [ gettering capacity ] if less [ if V/G becomes smaller than  $0.190 \text{ mm}^2 / \text{near K-min}$ , a BMD consistency will fall rapidly, and ] than  $0.175 \text{ mm}^2 / \text{K-min}$  An individual /  $\text{cm}^3$  It turns out that it falls to below. That is, in order to obtain BMD of high density, V/G was understood [ more than  $0.175 \text{ mm}^2 / \text{K-min}$ , then ] are good irrespective of the location within a wafer side.

[0019] On the other hand, drawing 2 makes relative evaluation on the size of a grown-in defect by OPP (Optical Precipitate Profiler), and shows the result of having investigated relation with V/G. The relation of all the data of OPP size and V/G which were measured like drawing 1 about a center section, the R/2 section within the field of a wafer, and a periphery is shown, and it means that OPP size correlates V/G and directly. That is, in the range in which the size of a grown-in defect exceeds  $0.225 \text{ mm}^2 / \text{K-min}$  by V/G becoming small rapidly by below  $0.225 \text{ mm}^2 / \text{K-min}$ , it discovered newly that the size of a grown-in defect was in a saturation inclination with a big value. Therefore, what is necessary is not to be concerned with the location within the field of a wafer, but just to make V/G into below  $0.225 \text{ mm}^2 / \text{K-min}$ , in order to consider as a grown-in defect with the small size which is easy to extinguish by heat treatment.

[0020] As mentioned above, if V/G is manufactured so that it may become within the limits of  $0.175$ - $0.225 \text{ mm}^2 / \text{K-min}$  in the direction of a path of a crystal in case the CZ process silicon single crystal by which the nitrogen dope was carried out is pulled up from the result of drawing 1 and drawing 2, an ununiformity does not become in a wafer side, but since grown-in defect size is moderately small, the annealing wafer with which a grown-in defect is extinguished all over a wafer in rear-spring-supporter 10 minutes, and a moderate BMD consistency is formed will be obtained.

[0021] Here, in the periphery section of a pull-up crystal, the point defect which determines the size and the BMD consistency of a grown-in defect will carry out out-diffusion during crystal training. Therefore, in the field (when a crystal with a diameter of 200mm is pulled up, it is from a periphery edge to 10mm) from the periphery edge of a pull-up crystal to about 5% of a radius, correlation of the size and the BMD consistency of a grown-in defect, and V/G becomes weak. Namely, it is at least 90% of field except every 5% of both periphery sections of the direction of a path of a pull-up crystal that V/G in this invention is applied, and this field is changed in 90 - 100% of range according to pull-up conditions.

[0022]

[Embodiment of the Invention] Hereafter, the operation gestalt of this invention is explained to a detail, referring to a drawing. First, drawing 6 R> 6 explains the example of a configuration of the crystal pulling equipment by the CZ process used by this invention. As shown in drawing 6, this crystal pulling equipment 30 The pull-up room 31, the crucible 32 prepared all over the pull-up room 31, and the heater 34 arranged around a crucible 32, It has the reel style (not shown) which rotates or rolls round the crucible maintenance shaft 33 made to rotate a crucible 32 and its rolling mechanism (not shown), the seed chuck 6 holding the seed crystal 5 of silicon, the wire 7 that pulls up a seed chuck 6, and a wire 7, and is constituted. A quartz crucible is prepared in the side in which a crucible 32 holds the silicon melt (molten bath) 2 of the inside, and the graphite crucible is prepared in the outside. Moreover, the heat insulator 35 is arranged around [ outside ] the heater 34.

[0023] Moreover, what is necessary is just to perform the approach of expanding the proper range of V/G to the direction of a path, and shaft orientations as manufacture conditions in connection with the manufacture approach of this invention, by the approach already learned well. That is, the annular solid-liquid interface heat insulator 8 is formed in the periphery of the solid-liquid interface of a crystal, and HZ which has arranged the up surrounding heat insulator 9 is installed on it so that the difference (germanium-Gc) of the temperature gradient (germanium) of the crystal circumference and the temperature gradient (Gc) of a crystal center may be made small and the solid-liquid interface temperature gradient G may become a flat in a field. This solid-liquid interface heat insulator 8 forms the 3-5cm clearance 10 between that soffit and surface of hot water of silicon melt 2, and is installed in it. The up surrounding heat insulator 9 may not be used depending on conditions. Furthermore, coolant gas may be sprayed or the tubed cooling system 36 which interrupts radiant heat and cools a single crystal may be formed.

[0024] Independently, by installing the magnet which is not illustrated in the horizontal outside of the pull-up room 31, and impressing magnetic fields, such as a horizontal direction or a perpendicular direction, to silicon melt 2, the convection current of melt is controlled and, recently, the so-called MCZ method for measuring the stable growth of a single crystal is used in many cases.

[0025] Next, the single-crystal-growth approach by above crystal pulling equipment 30 is explained. First,

within a crucible 32, the high grade polycrystal raw material of silicon is heated more than the melting point (about 1420-degreeC), and is dissolved. A nitrogen dope can be performed by throwing in a silicon wafer with a nitride for example, in raw material silicon. Next, the head of seed crystal 5 is made contacted or immersed in the surface abbreviation core of melt 2 by beginning to roll a wire 7. Then, while rotating the crucible maintenance shaft 33 in the proper direction, single crystal growth is started by rolling round rotating a wire 7 and pulling up seed crystal 5. Henceforth, the single crystal rod 1 of an approximate circle column configuration can be obtained by adjusting a pull-up rate and temperature appropriately.

[0026] It can consider as a nitrogen dope silicon wafer by cutting down the obtained single crystal rod by a wire saw etc. by the usual approach, and giving beveling, wrapping, etching, polish, etc.

[0027] Next, in this invention, it heat-treats to the obtained silicon wafer. A defect-free layer is formed in a front face of this at the homogeneity within a field, and BMD occurs in high density by it at the bulk section. Heat treatments (for example, 1150 degree C, 4 etc. hours, etc.) of 1 hours or more are performed at 1000-1350 degrees C under inert gas, such as an argon, hydrogen gas, or these mixed ambient atmospheres, using the batch type furnace of the usual heater type as concrete heat treatment conditions. Moreover, using the RTA (Rapid Thermal Annealing) equipment by lamp heating etc., heat treatment by rapid heating and forced cooling can be performed, or it can also consider as heat treatment which used together a batch type furnace and RTA equipment.

[0028]

[Example] Although the example and the example of a comparison of this invention are given and this invention is explained concretely hereafter, this invention is not limited to these.

(Example 1) as an example 1 -- crystal center temperature gradient  $G_c = 3.543$  [K/mm] and crystal ambient temperature inclination germanium =  $3.933$  [K/mm] and germanium- $G_c = 0.390$  [K/mm] and the crystal pulling equipment which has HZ with comparatively small germanium- $G_c$ , the pull-up rate was adjusted to about 0.74 mm/min, and the nitrogen dope silicon single crystal with a diameter of 6 inches was pulled up. A nitrogen dope throws in a silicon wafer with a nitride in raw material silicon, and the nitrogen concentration (calculated value) in the location of the shoulder of a pull-up crystal is  $2 \times 10^{13}$  /cm<sup>3</sup>. It was made to become. Moreover, the oxygen density was adjusted so that it might be set to 14 - 15ppma (JEIDA (Japan Electronic Industry Development Association) specification).

[0029] The crystal radial distribution of V/G at the time of crystal pulling were shown in drawing 3 . As for V/G, the whole close direction of a path was in the range of about 0.180-0.223mm<sup>2</sup> / K-min.

[0030] the crystal which was able to be pulled up to a silicon wafer -- producing -- OPP -- the precipitation heat treatment of 4-hour 800 degrees C after measuring the size of a grown-in defect by law and +1000 degrees C, and 16 hours -- adding -- BMD -- forming -- OPP -- the BMD consistency was measured by law. The measurement result of the size of a grown-in defect was shown in drawing 4 , and the measurement result of a BMD consistency was shown in drawing 5 .

[0031] The grown-in defect was the size (1.5 or less) which can fully be extinguished according to 1200 degrees C and the argon ambient atmosphere of 1 hour ( drawing 4 ), and was small. [ of field interior division cloth ] moreover, a BMD consistency -- the inside of a wafer side -- which location -- also setting -- about two to  $5 \times 10^9$  /cm<sup>3</sup> it is -- high-density and uniform field interior division cloth was obtained ( drawing 5 ).

[0032] (The example 1 of a comparison, example 2 of a comparison) as the examples 1 and 2 of a comparison --  $G_c = 3.778$  [K/mm] and germanium =  $4.904$  [K/mm] and germanium- $G_c = 1.126$  [K/mm] and the crystal pulling equipment which has HZ with comparatively large germanium- $G_c$ , in the example 1 of a comparison, the raising rate was adjusted to about 0.87 mm/min in about 0.84 mm/min and the example 2 of a comparison, and the nitrogen dope silicon single crystal with a diameter of 6 inches was pulled up. A nitrogen dope throws in a silicon wafer with a nitride in raw material silicon, and the nitrogen concentration (calculated value) in the location of the shoulder of a pull-up crystal is  $2 \times 10^{13}$  /cm<sup>3</sup>. It was made to become. Moreover, the oxygen density was adjusted so that it might be set to 14 - 15ppma (JEIDA).

[0033] The crystal radial distribution of V/G at the time of the crystal pulling of the example 1 of a comparison and the example 2 of a comparison were written together to drawing 3 . It was about 83% from the core of a crystal to the range of about 62mm that close V/G was in the range of 0.175-0.225mm<sup>2</sup> / K-min in the example 1 of a comparison, and, in the case of the example 2 of a comparison, it was about 48% from the location of about 30mm to the location of about 66mm in the direction of a periphery from the core of a crystal.

[0034] the crystal which was able to be pulled up to a silicon wafer -- producing -- OPP -- the precipitation

heat treatment of 4-hour 800 degrees C after measuring the size of a grown-in defect by law and +1000 degrees C, and 16 hours -- adding -- BMD -- forming -- OPP -- the BMD consistency was measured by law. To drawing 4, the measurement result of the size of a grown-in defect was written together, and the measurement result of a BMD consistency was written together to drawing 5.

[0035] In the example 1 of a comparison, grown-in defect size was small to some extent, and it was very small in a wafer periphery at the wafer core side, and although just the field interior division cloth of defective size was large, it was the defect of the size which is easy to disappear by annealing on the whole. However, about the BMD consistency after precipitation heat treatment, it sets to a wafer periphery with the low value of V/G, and a BMD consistency is  $2 \times 10^8$  /cm<sup>3</sup>. It is low with extent and it turned out that field interior division cloth with small gettering capacity is large at a periphery.

[0036] In the example 2 of a comparison, it is related with a BMD consistency, and is about  $1 \times 10^9$  /cm<sup>3</sup> in a field. Although the above was obtained, the field interior division cloth of grown-in defect size was large, and since the size by the side of a wafer core was quite large, even if it performed annealing by 1200 degrees C and the argon ambient atmosphere of 1 hour, it checked especially that a part of grown-in defect for a core remained.

[0037] In order to make the size of a grown-in defect, and the both sides of a BMD consistency into the homogeneity within a field in HZ of the crystal pulling equipment used in the examples 1 and 2 of a comparison, these results will show that it is very difficult, even if it controls a pull-up rate in the range in which it was restricted to 0.84 - 0.87 mm/min.

[0038] In addition, this invention is not limited to the above-mentioned operation gestalt. The above-mentioned operation gestalt is instantiation, and no matter it may be what thing which has the same configuration substantially with the technical thought indicated by the claim of this invention, and does the same operation effectiveness so, it is included by the technical range of this invention.

[0039] For example, in the above-mentioned operation gestalt, although the example was given and explained per when a silicon single crystal with a diameter of 6 inches was raised, this invention is not limited to this but can be applied also to the diameter of 8-16 inches, or the silicon single crystal beyond it. Moreover, it cannot be overemphasized that this invention is applicable also to the so-called MCZ method for impressing a level magnetic field and length magnetic field, a cusp field, etc. to silicon melt.

[0040]

[Effect of the Invention] According to this invention, the field interior division cloth of grown-in defect size can also form the silicon wafer which doped nitrogen also with the uniform field interior division cloth of a BMD consistency. Therefore, if elevated-temperature heat treatment is performed to this, there is no variation within a field of the defect-free layer of the wafer surface section, and the annealing wafer with which a BMD consistency has uniform IG layer in a field in the bulk section can be manufactured.

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[Translation done.]

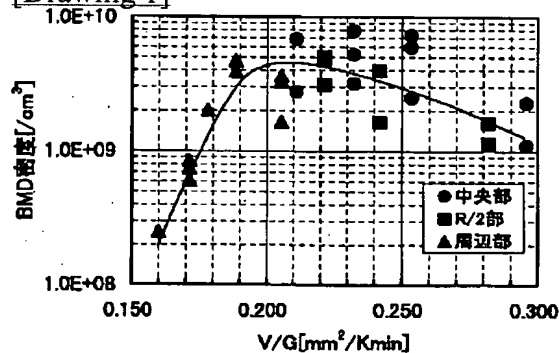
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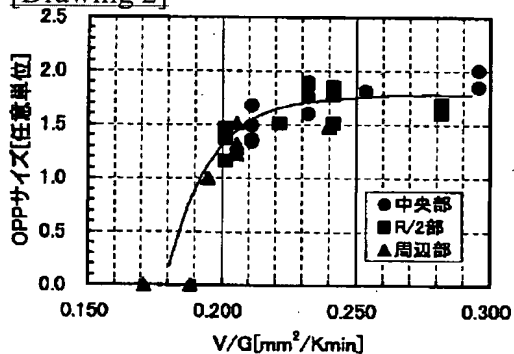
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## DRAWINGS

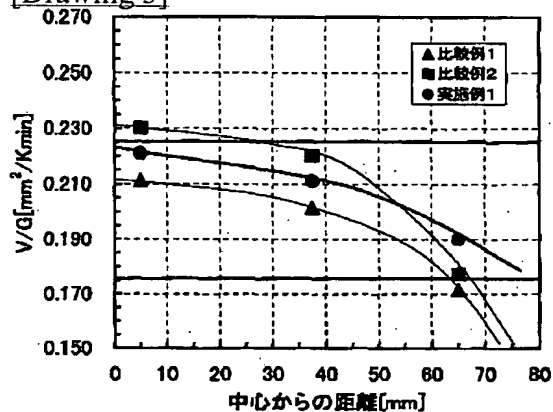
[Drawing 1]



[Drawing 2]

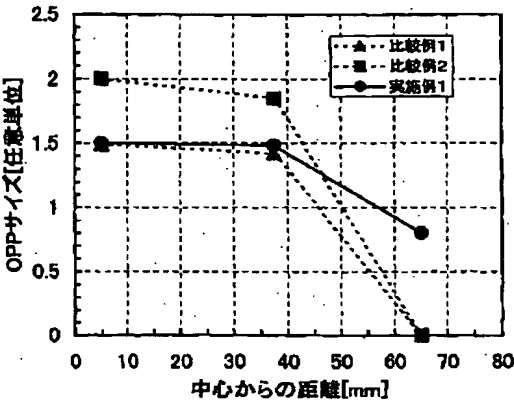


[Drawing 3]

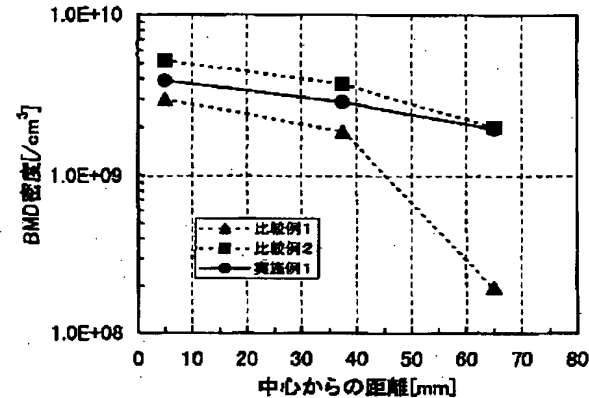


[Drawing 4]

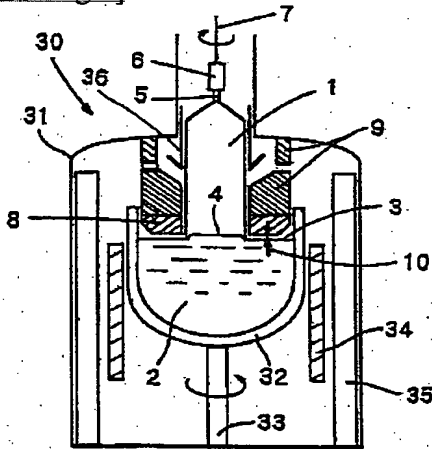




[Drawing 5]



[Drawing 6]



[Translation done.]

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**SOLUTION:** In the manufacturing method of a silicon wafer which forms the silicon wafer from a silicon single crystal pulled up after nitrogen is doped to the silicon single crystal by a CZ method and heat-treats the wafer, the wafer is grown on the condition that the ratio  $V/G$  of the pulling-up speed  $V$  (mm/min) at the time when the silicon single crystal is pulled up to a temperature gradient  $G$  (K/mm) in a solid-liquid interface is set in the ratio of 1 to 0.175 to 0.225 mm<sup>2</sup>/K.min in the extent wider than 90% in the radial direction of the pulled-up crystal and the wafer is formed by the manufacturing method.

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(54) 【発明の名称】 シリコンウエーハの製造方法

(57) 【要約】

【課題】 熱処理後のアニールウエーハに見られる無欠陥層の面内バラツキ（すなわち、グローニン欠陥サイズの面内バラツキ）と、析出熱処理またはデバイス熱処理等の熱処理後のBMD密度の面内バラツキを抑えて、十分な無欠陥層とBMD密度を面内均一に有するアニールウエーハを作製するために好適なシリコンウエーハを製造する方法およびそのようなシリコンウエーハを提供する。

【解決手段】 CZ法により窒素をドーブして引上げられたシリコン単結晶からシリコンウエーハを作製し、該シリコンウエーハに熱処理を施すシリコンウエーハの製造方法において、前記シリコン単結晶を引上げる際の引上速度 $V(\text{mm/min})$ と固液界面の温度勾配 $G(\text{K/mm})$ の比 $V/G$ が、引上げ結晶径方向の90%以上の範囲において $0.175 \sim 0.225 \text{ mm}^2/\text{K} \cdot \text{min}$ となる条件で育成するシリコンウエーハの製造方法とその製造方法で作製されたシリコンウエーハ。

## 【特許請求の範囲】

【請求項1】 チョクラスキー法により窒素をドーブして引上げられたシリコン単結晶からシリコンウエーハを作製し、該シリコンウエーハに熱処理を施すシリコンウエーハの製造方法において、前記シリコン単結晶を引上げる際の引上速度 $V$  (mm/min)と固液界面の温度勾配 $G$  (K/mm)の比 $V/G$ が、引上げ結晶径方向の90%以上の範囲において $0.175 \sim 0.225 \text{ mm}^2 / \text{K} \cdot \text{min}$ となる条件で育成することを特徴とするシリコンウエーハの製造方法。

【請求項2】 前記シリコンウエーハ中の窒素濃度が $1 \times 10^{13} \sim 5 \times 10^{15} \text{ 個/cm}^3$ であることを特徴とする請求項1に記載したシリコンウエーハの製造方法。

【請求項3】 前記請求項1または請求項2に記載した製造方法により製造されたことを特徴とするシリコンウエーハ。

## 【発明の詳細な説明】

## 【0001】

【発明が属する技術分野】本発明は、窒素をドーブして引上げたチョクラスキー法(CZ法)シリコン単結晶から作製されたシリコンウエーハに熱処理(アニール)を施すことにより、ウエーハ表層部に無欠陥層を有し、バルク部にイントリンシックゲッタリング(IG, Intrinsic Gettering)層が形成されるシリコンウエーハ(アニールウエーハ)を製造するのに好適なシリコンウエーハの製造方法に関する。

## 【0002】

【従来の技術】半導体デバイスの高集積化・微細化に伴い、ウエーハ表層の一層の完全性とバルク中のゲッタリング能力の強化が強く要求されている。それに対し、最近、窒素をドーブしたCZ法シリコンウエーハに熱処理を施すことにより、上記の2つの要求を同時に満たしたウエーハが開発された。

【0003】すなわち、CZ法シリコン単結晶に窒素をドーブすることにより、as-grown結晶中のグローニン(grown-in)欠陥(主に原子空孔の集合体により形成されるボイド欠陥)のサイズが小さくなるため、後工程の高温アニールによりウエーハ表層部の無欠陥化が容易になり、しかもバルク部においては窒素が有する酸素析出促進効果により、析出熱処理やデバイス熱処理工程を経ることによって、ゲッタリングに寄与する酸素析出物等の欠陥(以下、BMD(Bulk Micro Defects)と呼ぶことがある)を高密度に有するIG層が形成されるというものである。

## 【0004】

【発明が解決しようとする課題】ところで、CZ法シリコンウエーハのバルク部に形成され、ゲッタリングに寄与するBMDの密度と、表層部の無欠陥層の形成に影響するグローニン欠陥のサイズは、通常、面内分布を有することが知られており、特に、ウエーハの中心付近で

BMD密度、グローニン欠陥サイズともに大きく、ウエーハ周辺では両者とも徐々に低下している傾向がある。

【0005】この傾向は窒素ドーブ結晶においても同様で、BMD密度やグローニン欠陥サイズの絶対値は変化するが、面内分布を持つことには変わりはない。よって、表層部に無欠陥層を形成するための高温アニールを施した後は、アニールウエーハの中心部分に特にグローニン欠陥が残り易いことになる。

10 【0006】また、バルクのゲッタリング能力を決定する析出熱処理後のBMD密度に関し、ウエーハ周辺部でBMD密度が低下する傾向は、特に窒素ドーブウエーハに関して顕著であることが、本発明者の調査により明確になった。

【0007】このように、アニールウエーハに求められるウエーハ表層部に形成される無欠陥層と析出熱処理またはデバイス熱処理後のBMD密度のいずれの特性も、現時点では面内で不均一であるという問題を抱えている。

20 【0008】そこで本発明は、このような問題点を解決するためになされたもので、熱処理後のアニールウエーハに見られる無欠陥層の面内バラツキ(すなわち、グローニン欠陥サイズの面内バラツキ)と、析出熱処理またはデバイス熱処理等の熱処理後のBMD密度の面内バラツキを抑えて、十分な無欠陥層とBMD密度を面内均一に有するアニールウエーハを作製するために好適なシリコンウエーハを製造する方法およびそのようなシリコンウエーハを提供することを主たる目的としている。

## 【0009】

30 【課題を解決するための手段】上記目的を達成する本発明のシリコンウエーハの製造方法に係る発明は、チョクラスキー法により窒素をドーブして引上げられたシリコン単結晶からシリコンウエーハを作製し、該シリコンウエーハに熱処理を施すシリコンウエーハの製造方法において、前記シリコン単結晶を引上げる際の引上速度 $V$  (mm/min)と固液界面の温度勾配 $G$  (K/mm)の比 $V/G$ が、引上げ結晶径方向の90%以上の範囲において $0.175 \sim 0.225 \text{ mm}^2 / \text{K} \cdot \text{min}$ となる条件で育成することを特徴としている(請求項1)。

40 【0010】このような条件下で育成された窒素をドーブしたシリコン単結晶から切り出されたシリコンウエーハは、グローニン欠陥サイズの面内分布もBMD密度の面内分布も均一なものとすることができる。従って、これに高温熱処理を施せば、ウエーハ表層部の無欠陥層の面内バラツキがなく、バルク部のBMD密度が面内均一で高密度なIG能力の高いアニールウエーハを得ることができる。

50 【0011】この場合、前記シリコンウエーハ中の窒素濃度は、 $1 \times 10^{13} \sim 5 \times 10^{15} \text{ 個/cm}^3$ であることが好ましい(請求項2)。窒素濃度をこのような範囲内

に納めれば、グローニン欠陥のサイズを小さくする効果が十分であるとともに、単結晶の育成にも悪影響を及ぼさないで、後工程の高温アニールによりウエーハ表層部の無欠陥化が容易になるとともに、バルク部においては窒素が有する酸素析出促進効果により、析出熱処理やデバイス熱処理を経ることによって、ゲッタリングに寄与するBMDを高密度に有するIG層を形成することができる。

【0012】そして本発明によれば、熱処理後のアニールウエーハに見られる無欠陥層の面内バラツキと、析出熱処理またはデバイス熱処理等の熱処理後のBMD密度の面内バラツキを抑えて、十分な無欠陥層とBMD密度を面内均一に有するアニールウエーハを得ることのできるシリコンウエーハが提供される(請求項3)。

【0013】以下、本発明についてさらに詳細に説明する。本発明者は、十分な無欠陥層とBMD密度を面内均一に有するアニールウエーハを作製するためには、シリコンウエーハとして、バルク部に形成されるゲッタリングに寄与するBMDの密度と、表層部の無欠陥層の形成に影響するグローニン欠陥のサイズがともに面内分布を持たないものを用意する必要があることを知見した。

【0014】すなわち本発明者は、アニールウエーハ用として現状製造している窒素ドーパされたCZ法シリコンウエーハに高温アニールを施した後のウエーハ表層部のグローニン欠陥密度と、追加熱処理後のBMD密度に関して鋭意調査を行った。その結果、ウエーハ中心部では残存欠陥数は多く、BMD密度も高いが、ウエーハ周辺部では残存欠陥数は少なく、BMD密度も少ないことがわかった。また、その中間の位置(以下、R/2位置という。Rはウエーハ半径)では、残存欠陥も程々に少なく、BMD密度も程々に高くなっていた。

【0015】これら3箇所の中ではR/2位置が、表層部の完全性とバルク中のゲッタリング能力のバランスが最も良いことになる。つまり、このR/2位置の状態をウエーハ面内に拡大できれば、面内均一で高品質なウエーハが得られることになる。そこで、このR/2位置の状態を拡大するため、BMDやグローニン欠陥の分布とCZ法シリコン単結晶の引上げ方法との相関関係を調査した。

【0016】その結果、このようにグローニン欠陥サイズやBMD密度の面内分布が不均一になる原因は、少なくとも結晶育成時の引上げ速度V(mm/min)とシリコンの融点から1400℃までの範囲における引き上げ軸方向の固液界面の温度勾配G(K/mm)の比であるV/Gが面内で分布を持つ、すなわちV/Gが面内で変動するためであることがわかってきた。そこでウエーハ面内の位置に関わらずグローニン欠陥サイズやBMD密度を所望のものとするために必要な具体的なV/G値を求めることにした。以下、これについて説明する。

【0017】グローニン欠陥がV/Gの影響を受けることは既に良く知られているので、結晶引上げ装置の特定のホットゾーン(Hot Zone、HZ、炉内構造)を用いて引上げ結晶中に取り込まれる窒素濃度を $1 \times 10^{13}$ 個/cm<sup>3</sup>とし、1.0~1.4mm/minの範囲から選択された引上げ速度にて複数本の結晶の育成を行い、それぞれのV/Gの面内分布とグローニン欠陥のサイズとの関係及び800℃×4時間+1000℃×16時間の熱処理後のBMD密度との関係を調査した。その結果を図1および図2に示す。

【0018】図1はウエーハの面内の中央部、R/2部、周辺部(ウエーハ外周より10mmの位置)について測定したBMD密度の全データとV/Gとの関係を示しており、BMD密度がV/Gと直接相関していることを表している。V/Gが0.190mm<sup>2</sup>/K・min付近より小さくなるとBMD密度が急激に低下し、0.175mm<sup>2</sup>/K・minを下回るとゲッタリング能力が不十分となる $1 \times 10^9$ 個/cm<sup>3</sup>以下に低下することがわかる。すなわち、高密度のBMDを得るためには、ウエーハ面内位置にかかわらず、V/Gを0.175mm<sup>2</sup>/K・min以上とすれば良いことがわかった。

【0019】一方、図2はOPP(Optical Precipitate Profiler)によりグローニン欠陥のサイズを相対評価し、V/Gとの関係を調査した結果を示している。図1と同様にウエーハの面内の中央部、R/2部、周辺部について測定したOPPサイズの全データとV/Gとの関係を示しており、OPPサイズがV/Gと直接相関していることを表している。すなわち、V/Gが0.225mm<sup>2</sup>/K・min以下ではグローニン欠陥のサイズが急激に小さくなり、0.225mm<sup>2</sup>/K・minを越えるような範囲では、グローニン欠陥のサイズが大きな値で飽和傾向にあることを新規に発見した。従って、熱処理により消滅させ易いサイズの小さいグローニン欠陥とするためには、ウエーハの面内の位置に関わらず、V/Gを0.225mm<sup>2</sup>/K・min以下とすればよい。

【0020】以上、図1および図2の結果から、窒素ドーパされたCZ法シリコン単結晶を引上げる際に、V/Gを結晶の径方向で0.175~0.225mm<sup>2</sup>/K・minの範囲内となるように製造すれば、ウエーハ面内で不均一とはならず、グローニン欠陥サイズが適度に小さいためウエーハ全面にわたり十分にグローニン欠陥を消滅させ、かつ、適度なBMD密度が形成されるアニールウエーハが得られることになる。

【0021】ここで、引上げ結晶の外周部においては、グローニン欠陥のサイズやBMD密度を決める点欠陥が、結晶育成中に外方拡散してしまう。従って、引上げ結晶の外周端から半径の5%程度までの領域(例えば、直径200mmの結晶を引上げた場合には外周端から1

0mmまで)においては、グローンイン欠陥のサイズやBMD密度とV/Gの相関が弱くなる。すなわち、本発明におけるV/Gが適用されるのは、引上げ結晶の径方向の両外周部5%づつを除く、少なくとも90%の領域であり、この領域は引上げ条件により90~100%の範囲で変動する。

【0022】

【発明の実施の形態】以下、本発明の実施形態について、図面を参照しながら詳細に説明する。まず、本発明で使用したCZ法による単結晶引上げ装置の構成例を図6により説明する。図6に示すように、この単結晶引上げ装置30は、引上げ室31と、引上げ室31中に設けられたルツボ32と、ルツボ32の周囲に配置されたヒータ34と、ルツボ32を回転させるルツボ保持軸33及びその回転機構(図示せず)と、シリコンの種結晶5を保持するシードチャック6と、シードチャック6を引上げるワイヤ7と、ワイヤ7を回転又は巻き取る巻取機構(図示せず)を備えて構成されている。ルツボ32は、その内側のシリコン融液(湯)2を収容する側には石英ルツボが設けられ、その外側には黒鉛ルツボが設けられている。また、ヒータ34の外側周囲には断熱材35が配置されている。

【0023】また、本発明の製造方法に関わる製造条件として、V/Gの適正な範囲を径方向および軸方向に拡大する方法は既に良く知られている方法で行えばよい。即ち、結晶周辺の温度勾配(Ge)と結晶中心の温度勾配(Gc)の差(Ge-Gc)を小さくして固液界面温度勾配Gが面内でフラットになるように、例えば結晶の固液界面の外周に環状の固液界面断熱材8を設け、その上に上部囲繞断熱材9を配置したHZを設置している。この固液界面断熱材8は、その下端とシリコン融液2の湯面との間に3~5cmの隙間10を設けて設置されている。上部囲繞断熱材9は条件によっては使用しないこともある。さらに、冷却ガスを吹き付けたり、放射熱を遮って単結晶を冷却する筒状の冷却装置36を設けてもよい。

【0024】別に、最近では引上げ室31の水平方向の外側に、図示しない磁石を設置し、シリコン融液2に水平方向あるいは垂直方向等の磁場を印加することによって、融液の対流を抑制し、単結晶の安定成長をはかる、いわゆるMCZ法が用いられることも多い。

【0025】次に、上記の単結晶引上げ装置30による単結晶育成方法について説明する。まず、ルツボ32内でシリコンの高純度多結晶原料を融点(約1420°C)以上に加熱して融解する。窒素ドーブは、例えば原料シリコン中に窒化膜付きシリコンウエーハを投入することによって行うことができる。次に、ワイヤ7を巻き出すことにより融液2の表面略中心部に種結晶5の先端を接触又は浸漬させる。その後、ルツボ保持軸33を適宜の方向に回転させるとともに、ワイヤ7を回転させな

がら巻き取り種結晶5を引上げることにより、単結晶育成が開始される。以後、引上げ速度と温度を適切に調節することにより略円柱形状の単結晶棒1を得ることができる。

【0026】得られた単結晶棒を通常の方法により、ワイヤーソー等で切り出し、面取り、ラッピング、エッチング、研磨等を施すことによって、窒素ドーブシリコンウエーハとすることができる。

【0027】次に、本発明では、得られたシリコンウエーハに熱処理を施す。これによって表面に面内均一に無欠陥層が形成され、バルク部には高密度にBMDが発生する。具体的な熱処理条件としては、通常のヒータ式のバッチ炉を用い、アルゴン等の不活性ガス、水素ガス、またはこれらの混合雰囲気下で、1000~1350°Cで1時間以上の熱処理(例えば、1200°C・1時間、または1150°C・4時間等)を行う。また、ランプ加熱等によるRTA(Rapid Thermal Annealing)装置を用いて、急速加熱・急速冷却による熱処理を行ったり、バッチ炉とRTA装置を併用した熱処理とすることもできる。

【0028】

【実施例】以下、本発明の実施例と比較例を挙げて本発明を具体的に説明するが、本発明はこれらに限定されるものではない。

(実施例1) 実施例1として、結晶中心温度勾配Gc=3.543[K/mm]、結晶周辺温度勾配Ge=3.933[K/mm]、Ge-Gc=0.390[K/mm]と比較的Ge-Gcの小さいHZを有する単結晶引上げ装置を用い、引上げ速度を約0.74mm/minに調整して、直径6インチの窒素ドーブシリコン単結晶を引上げた。窒素ドーブは、原料シリコン中に窒化膜付きシリコンウエーハを投入し、引上げ結晶の肩の位置での窒素濃度(計算値)が $2 \times 10^{11}/\text{cm}^3$ となるようにした。また、酸素濃度は14~15ppma(JEIDA(日本電子工業振興協会)規格)となるように調整した。

【0029】図3に結晶引上げ時のV/Gの結晶径方向の分布を示した。V/Gは径方向全体が約0.180~0.223mm<sup>2</sup>/K・minの範囲に入っていた。

【0030】引上げられた結晶からシリコンウエーハを作製し、OPP法によりグローンイン欠陥のサイズを測定した後、800°C、4時間+1000°C、16時間の析出熱処理を加えてBMDを形成し、OPP法によりBMD密度を測定した。グローンイン欠陥のサイズの測定結果を図4に、BMD密度の測定結果を図5に示した。

【0031】グローンイン欠陥は、1200°C、1時間のアルゴン雰囲気により十分に消滅させることができるサイズ(1.5以下)であり(図4)、面内分布も小さかった。また、BMD密度は、ウエーハ面内いずれの位置においても、ほぼ $2 \sim 5 \times 10^9/\text{cm}^3$ であり、高密

度でかつ均一な面内分布が得られた(図5)。

【0032】(比較例1、比較例2)比較例1、2として、 $G_c = 3.778$  [K/mm]、 $G_e = 4.904$  [K/mm]、 $G_e - G_c = 1.126$  [K/mm]と比較的 $G_e - G_c$ の大きいHZを有する単結晶引上げ装置を用い、比較例1では引上速度を約0.84 mm/min、比較例2では約0.87 mm/minに調整して、直径6インチの窒素ドーブシリコン単結晶を引上げた。窒素ドーブは、原料シリコン中に窒化膜付きシリコンウエーハを投入し、引上げ結晶の肩の位置での窒素濃度(計算値)が $2 \times 10^{11} / \text{cm}^3$ となるようにした。また、酸素濃度は14~15 ppma (JEIDA)となるように調整した。

【0033】比較例1、比較例2の結晶引上げ時のV/Gの結晶径方向の分布を図3に併記した。比較例1でV/Gが0.175~0.225 mm<sup>2</sup>/K・minの範囲に入っていたのは、結晶の中心から約62 mmの範囲までの約83%であり、比較例2の場合は、結晶の中心から外周方向に約30 mmの位置から約66 mmの位置までの約48%であった。

【0034】引上げられた結晶からシリコンウエーハを作製し、OPP法によりグローンイン欠陥のサイズを測定した後、800℃、4時間+1000℃、16時間の析出熱処理を加えてBMDを形成し、OPP法によりBMD密度を測定した。グローンイン欠陥のサイズの測定結果を図4に、BMD密度の測定結果を図5に併記した。

【0035】比較例1ではウエーハ中心側においてグローンイン欠陥サイズがある程度小さく、ウエーハ周辺部では極めて小さくなっており、欠陥サイズの面内分布こそ大きい、全体的にアニールにより消え易いサイズの欠陥であった。しかしながら、析出熱処理後のBMD密度に関してはV/Gの値が低いウエーハ周辺部においてBMD密度が $2 \times 10^8 / \text{cm}^3$ 程度と低くなっており、周辺部でゲッター能力の小さい、面内分布が大きいものであることがわかった。

【0036】比較例2では、BMD密度に関しては面内では $1 \times 10^8 / \text{cm}^3$ 以上が得られたが、グローンイン欠陥サイズの面内分布が大きく、特にウエーハ中心側のサイズがかなり大きいため、1200℃、1時間のアルゴン雰囲気によるアニールを行っても中心部分のグローンイン欠陥が一部残留することを確認した。

【0037】これらの結果より、比較例1、2で使った結晶引上げ装置のHZの場合、グローンイン欠陥のサイズとBMD密度の双方を面内均一にするためには、た

とえ引上げ速度を0.84~0.87 mm/minに限られた範囲に制御したとしても極めて困難であることがわかる。

【0038】なお、本発明は、上記実施形態に限定されるものではない。上記実施形態は、例示であり、本発明の特許請求の範囲に記載された技術的思想と実質的に同一な構成を有し、同様な作用効果を奏するものは、いかなるものであっても本発明の技術的範囲に包含される。

【0039】例えば、上記実施形態においては、直径6インチのシリコン単結晶を育成する場合につき例を挙げたが、本発明はこれには限定されず、直径8~16インチあるいはそれ以上のシリコン単結晶にも適用できる。また、本発明は、シリコン融液に水平磁場、縦磁場、カスプ磁場等を印加するいわゆるMCZ法にも適用できることは言うまでもない。

【0040】

【発明の効果】本発明によれば、グローンイン欠陥サイズの面内分布もBMD密度の面内分布も均一な窒素をドーブしたシリコンウエーハを形成することができる。従って、これに高温熱処理を施せば、ウエーハ表層部の無欠陥層の面内バラツキがなく、バルク部にBMD密度が面内均一なIG層を有するアニールウエーハを製造することができる。

【図面の簡単な説明】

【図1】本発明におけるV/GとBMD密度との関係を示す図である。

【図2】本発明におけるV/Gとグローンイン欠陥サイズとの関係を示す図である。

【図3】実施例1、比較例1、比較例2に関し、結晶引上げ時の結晶径方向におけるV/Gの分布図である。

【図4】実施例1、比較例1、比較例2に関し、引上げ結晶の結晶径方向におけるグローンイン欠陥サイズの分布図である。

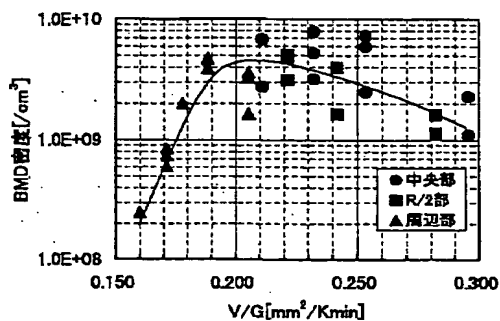
【図5】実施例1、比較例1、比較例2に関し、引上げ結晶の結晶径方向におけるBMD密度の分布図である。

【図6】本発明で使用したCZ法による単結晶引上げ装置の概略説明図である。

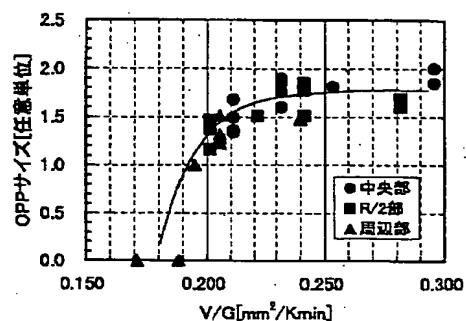
【符号の説明】

1…成長単結晶棒、 2…シリコン融液、 3…湯面、 4…固液界面、 5…種結晶、 6…シードチャック、 7…ワイヤ、 8…固液界面断熱材、 9…上部囲繞断熱材、 10…湯面と固液界面断熱材下端との隙間、 30…単結晶引上げ装置、 31…引上げ室、 32…ルツボ、 33…ルツボ保持軸、 34…ヒータ、 35…断熱材、 36…冷却装置。

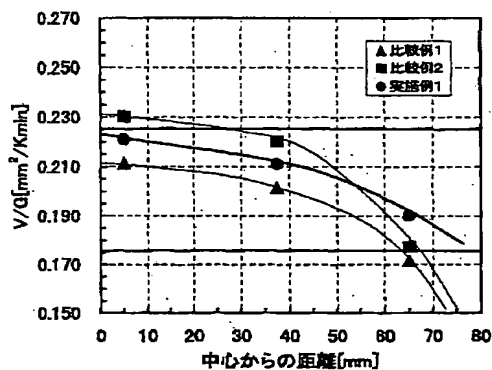
【図1】



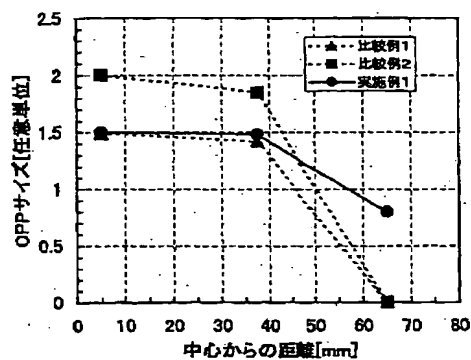
【図2】



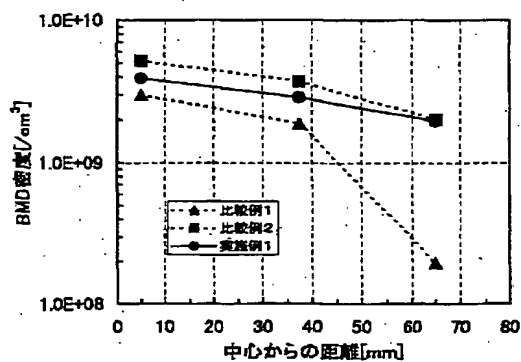
【図3】



【図4】



【図5】



【図6】

